Supporting Information

Nanogap engineering of 3D nanoraspberries into 2D plasmonic nanoclusters toward improved SERS performance

Jian Yang[a], Xinxing Zhang [a], Lin Geng[a], Chao Xia[a], Xin Chen[a], Wenzhong Yang[a], Hui Xu*[,a] and Zhiqun Lin*[,b]

[a]Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China. Email: ias_hxu@njtech.edu.cn.

[b]Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore, 117585 Singapore. Email:z.lin@nus.edu.sg.

Experimental section

1.1 Materials

Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%), tris[2-(dimethylamino)ethyl]amine (Me_6TREN, 99%), ammonia, sodium citrate (99%), copper bromide (CuBr, 98%), 4-vinylpyridine (4VP, 98%), and 4-mercaptobenzoic acid (4-MBA) were supplied by Sigma-Aldrich. Hydrofluoric acid (50%), trichloro-[4-(chloromethyl)phenyl]silane (97%), tetraethyl orthosilicate (TEOS, 98%), and divinylbenzene (DVB) were purchased from Alfa Aesar. Malachite green (MG), technical grade ethanol, *N,N*-dimethylformamide (DMF), and tetrahydrofuran (THF) were supplied by Wanqing Chemical Glassware Instruments Co., Ltd. (Nanjing, China).

1.2 Characterization

Scanning electron microscopy (SEM) was performed on a SU-70 FESEM at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) was measured on a JEM-1400 (JEOL) operating at 100 kV. Atomic Force Microscope (AFM) analysis was performed on a Bruker dimensional icons. The ultraviolet-visible (UV-vis) absorption spectra of the samples were measured on a λ 750 UV-vis spectrophotometer at room temperature. Raman scattering signals were examined using a PeakSeekerTM Raman spectrometer with a semiconductor laser (290 mW) at the wavelength of 785 nm as the excitation source.

1.3 Synthesis of SiO_2-*g*-P(4VP-*co*-DVB)

The atom transfer radical polymerization (ATRP) initiator SiO_2-Cl was synthesized

according to our previously reported work.[1] 200 mg SiO_2-Cl, 5 mL 4VP, 25 mg DVB, 5 mL DMF, 32 mg CuBr, and 50 mg Me_6TREN were added into an ampule and then evacuated and back-filled with argon through three freeze-thaw cycles. The reaction mixture was reacted at 50 °C for 48 h. The product was precipitated by hexane and then washed with ethanol three times. The resulting SiO_2-*g*-P(4VP-*co*-DVB) was dried under vacuum at 40 °C for 24 h.

1.4 Synthesis of AuNPs with an average diameter of ~30 nm

Typically, 0.0971 g of sodium citrate (CA) was dissolved in 150 mL of deionized water and boiled at 130 °C in an autoclave (Anhui Chemical Instruments Co., Ltd.). Then, 1 mL of 23 mM $HAuCl_4$ was added to the autoclave and heated at 130 °C for 10 min. The temperature was lowered to 90 °C. 1 mL of 60 mM CA solution was added, and 1 mL of 25 mM $HAuCl_4$ solution was added after 2 min. The above operation of adding CA and $HAuCl_4$ was repeated 7 times to obtain ~30 nm AuNPs. The product was collected by centrifugation and washed once with water.

1.5 Synthesis of SiO_2-*g*-P(4VP-*co*-DVB)/AuNPs nanoraspberry

1.0 mg of SiO_2-*g*-P(4VP-*co*-DVB) composite was dispersed in 10 mL of aqueous solution. 2.5 mL of AuNPs solution was added and the mixture was stirred for 5 min. After washing with ethanol three times, the SiO_2-*g*-P(4VP-*co*-DVB)/AuNPs nanoraspberry was collected by centrifugation and redispersed in 1.5 mL of ethanol to obtain SiO_2-*g*-P(4VP-*co*-DVB)/AuNPs dispersion solution.

1.6 Fabrication of P(4VP-*co*-DVB)/AuNPs nanocluster

The above-mentioned 10 μL of SiO_2-*g*-P(4VP-*co*-DVB)/AuNPs dispersion solution

was dropped on a silicon wafer. After the ethanol on the silicon wafer had completely evaporated at room temperature, the silicon wafer was placed in the center of a sealed petri dish. Then, 200 μL of 50% HF solution was dropped uniformly around the silicon wafer without contacting it. In the closed system, the SiO_2 core was etched by the volatile HF for 2h, leading to the P(4VP-*co*-DVB)/AuNPs nanoclusters.

1.7 SERS measurements

For the SERS characterization, the prepared SiO_2-*g*-P(4VP-*co*-DVB)/AuNPs nanoclusters were deposited on clean silicon wafers (0.3cm × 0.3cm), air dried, and incubated for 10 min with aqueous solutions of analyte molecules dropwise on the wafers so that the analyte molecules were effectively trapped on the surface of the nanoclusters. For water-soluble probe molecules, the unadsorbed probe molecules are washed away with water before Raman detection. The insoluble probe molecules were rinsed with methanol as solvent. Each spectrum was acquired at 15 randomly selected spots on the SERS substrate with an acquisition time of 3 s. Subsequently, HF was added to etch the SiO_2 and the resulting P(4VP-*co*-DVB)/AuNPs nanoclusters were subjected to the same SERS signal acquisition test.

1.8 Enhancement factor (EF) calculation

To determine and compare the enhancement factor (EF) of the prepared SiO_2-*g*-P(4VP-*co*-DVB)/AuNPs nanoraspberry and P(4VP-*co*-DVB)/AuNPs nanocluster as the SERS substrates, their EF values are estimated from Equation (S1):

$$EF = \frac{I_{SERS} N_{NR}}{I_{NR} N_{SERS}} \quad \text{(S1)}$$

where I_{SERS} and I_{NR} are the Raman intensities at 1077 cm^{-1} of the SERS and bulk mode, respectively. N_{SERS} and N_{NR} were the number of 4-MBA molecules adsorbed on SERS substrate and in the bulk irradiated by laser focusing spot under SERS and normal Raman conditions, respectively.

N_{SERS} and N_{NR} can be obtained according to the reported method.[2]

$$N_{SERS} = C_{4-MBA} \times V_{4-MBA} \times N_A \times \frac{S_{Laser\ spot\ area}}{S_{substrate}}$$

Where $C_{4\text{-}MBA}$ and $V_{4\text{-}MBA}$ are the density of 4-MBA and sample volume，$S_{laser\ spot\ area}$ and $S_{substrate}$ are the area of laser spot and the substrate.

Taking the laser spot diameter (about 1 μm), the penetration depth (about 2 μm), the molecule weight of solid 4-MBA (1.345 g/cm^3) into account,

$$N_{NR} = \frac{W_{4-MBA} \times N_A \times S_{Laser\ spot\ area} \times L_{penetration\ depth}}{M_{4-MBA}}$$

Where $W_{4\text{-}MBA}$ is the molecule weight of solid 4-MBA and $M_{4\text{-}MBA}$ is the molar mass of 4-MBA.

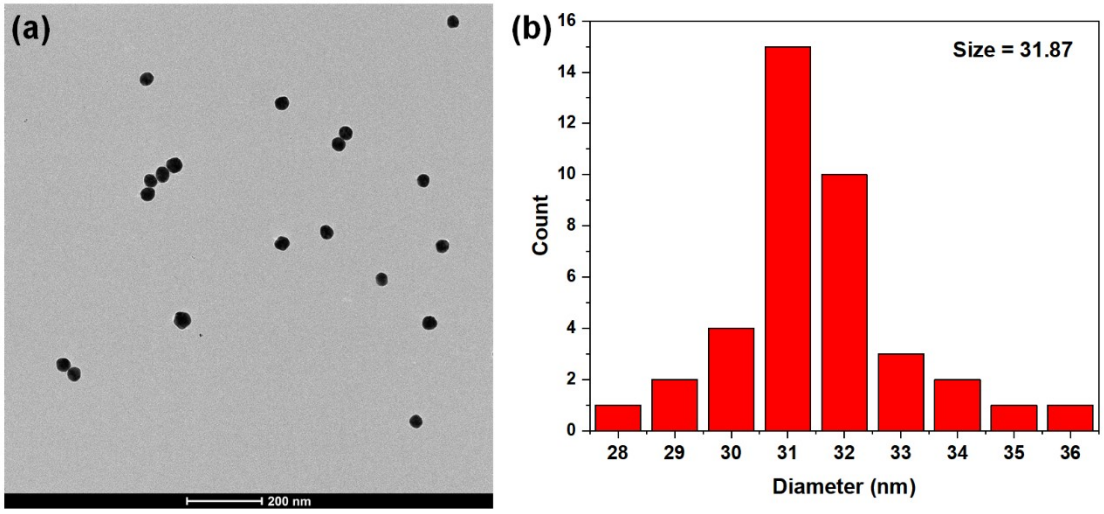

Figure S1. (a) TEM image of the AuNPs. (b) Size distribution histogram of the AuNPs with an average size of 31.87 nm.

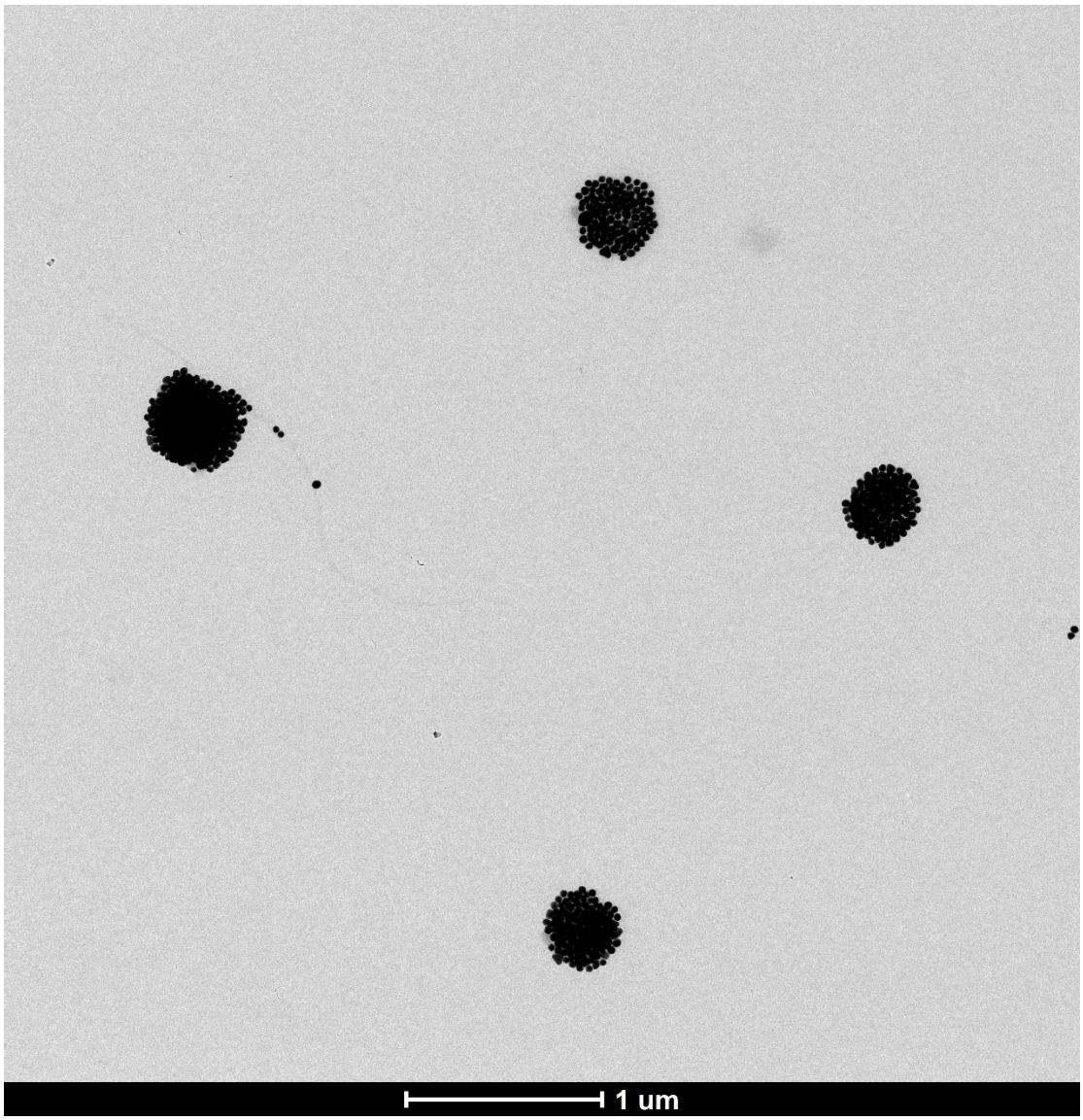

Figure S2. (a) TEM image of the P(4VP-*co*-DVB)/AuNPs nanoclusters.

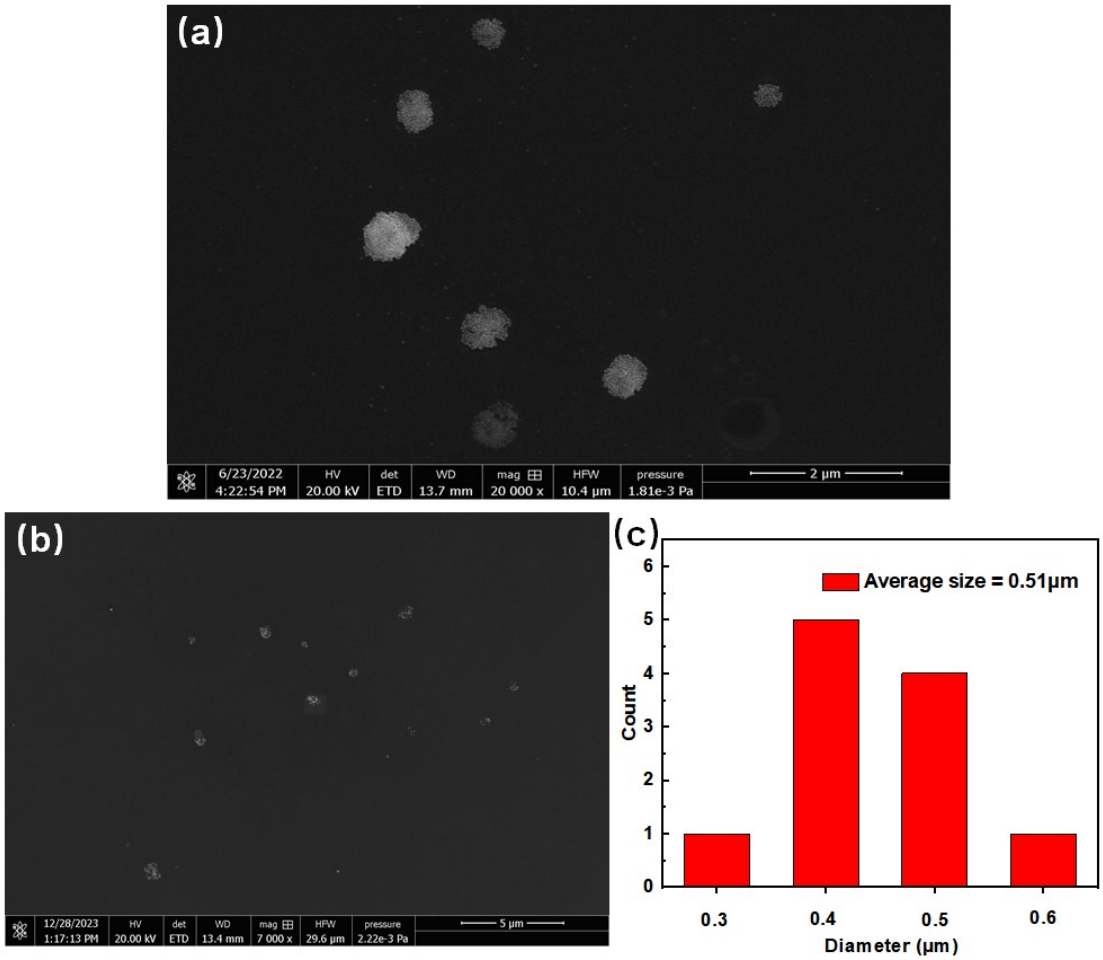

Figure S3. SEM image of the P(4VP-*co*-DVB)/AuNPs nanoclusters (a) scale bar 2 µm, (b) scale bar 5 µm, and the size distribution of the nanoclusters.

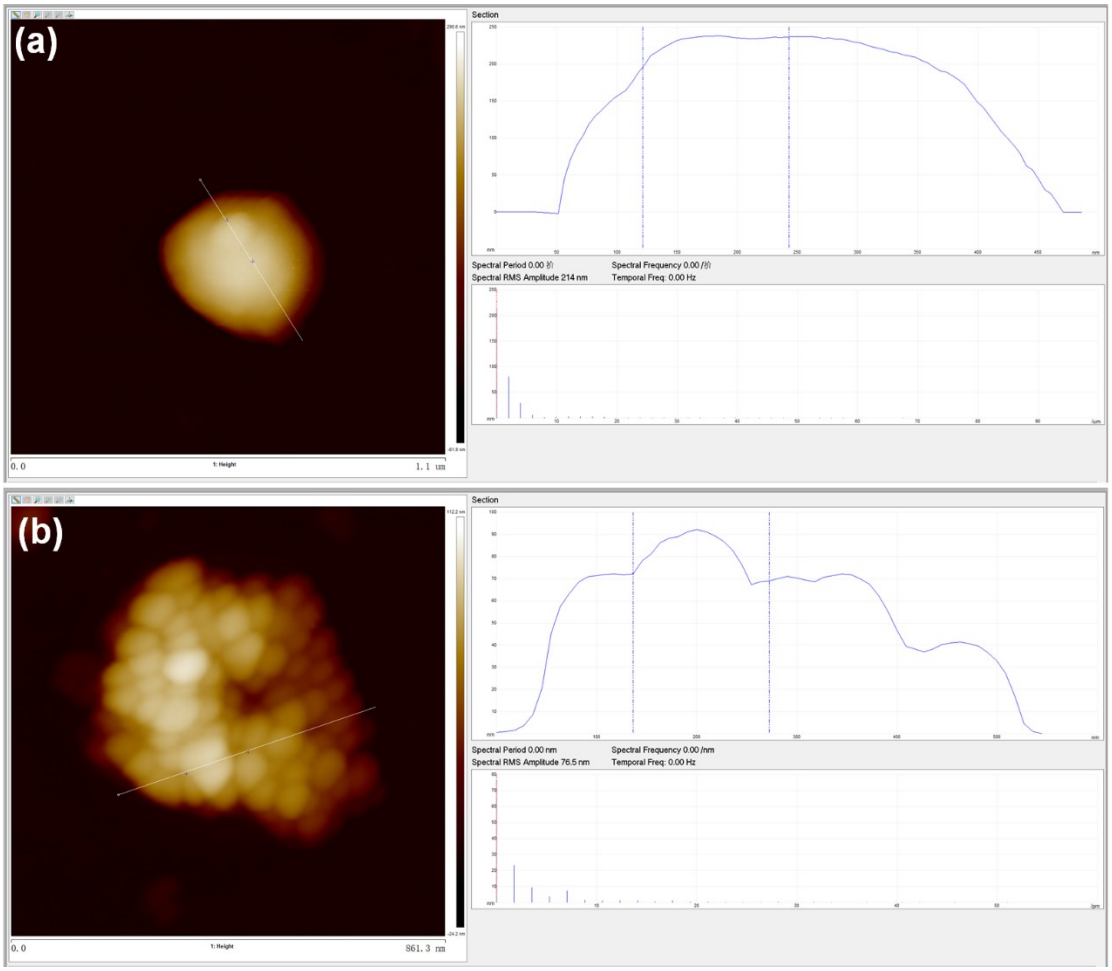

Figure S4. AFM images and their corresponding height profiles of (a) SiO_2-*g*-P(4VP-*co*-DVB)/AuNPs nanoraspberry and (b) P(4VP-*co*-DVB)/AuNPs nanocluster.

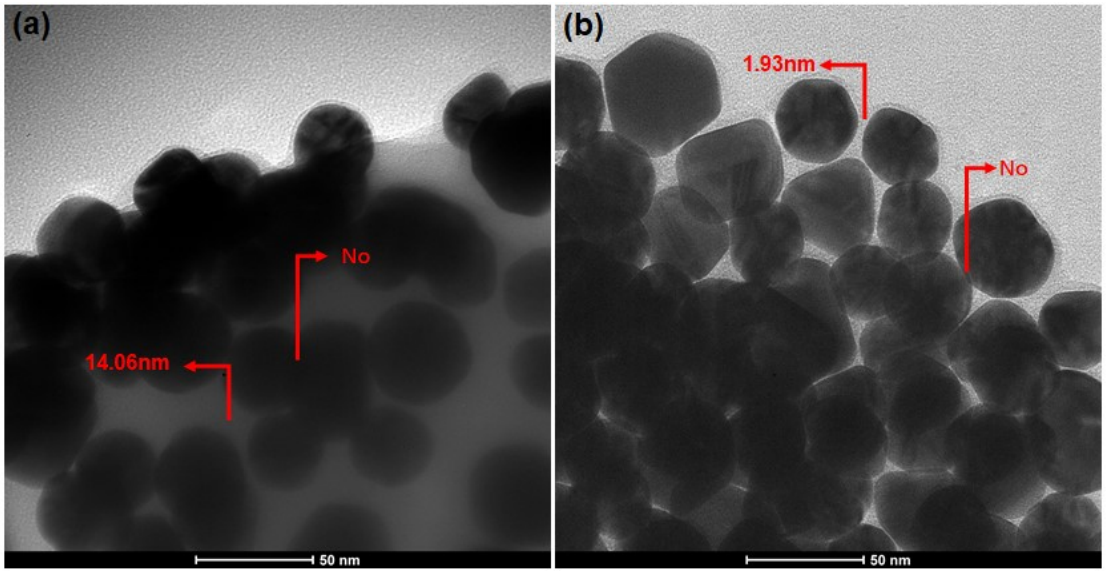

Figure S5. Representative high resolution TEM images of (a) SiO_2-*g*-P(4VP-*co*-DVB)/AuNPs and (b) P(4VP-*co*-DVB)/AuNPs.

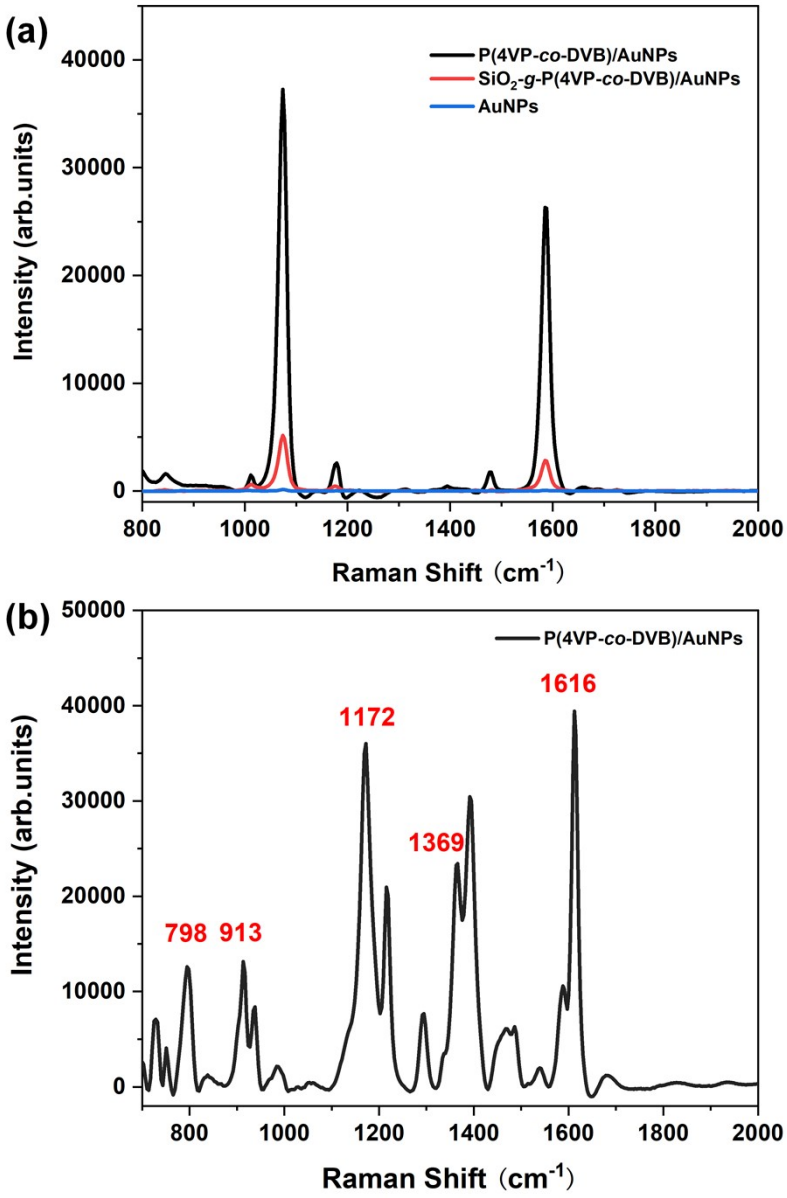

Figure S6. (a) SERS spectra of bare AuNPs (~31.87 nm), SiO_2-*g*-P(4VP-*co*-DVB)/AuNPs and P(4VP-*co*-DVB)/AuNPs tagged with 1.0 mM of 4-MBA. (b) SERS spectrum of 1.0 mM of MG absorbed on the P(4VP-*co*-DVB)/AuNPs nanocluster.

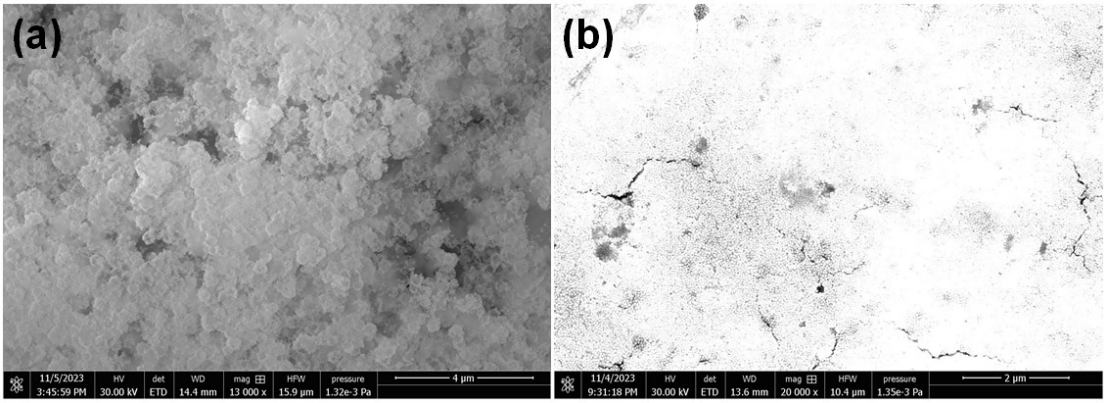

Figure S7. SEM images of (a) SiO_2-*g*-P(4VP-*co*-DVB)/AuNPs nanoraspberry and (b) P(4VP-*co*-DVB)/AuNPs nanocluster.

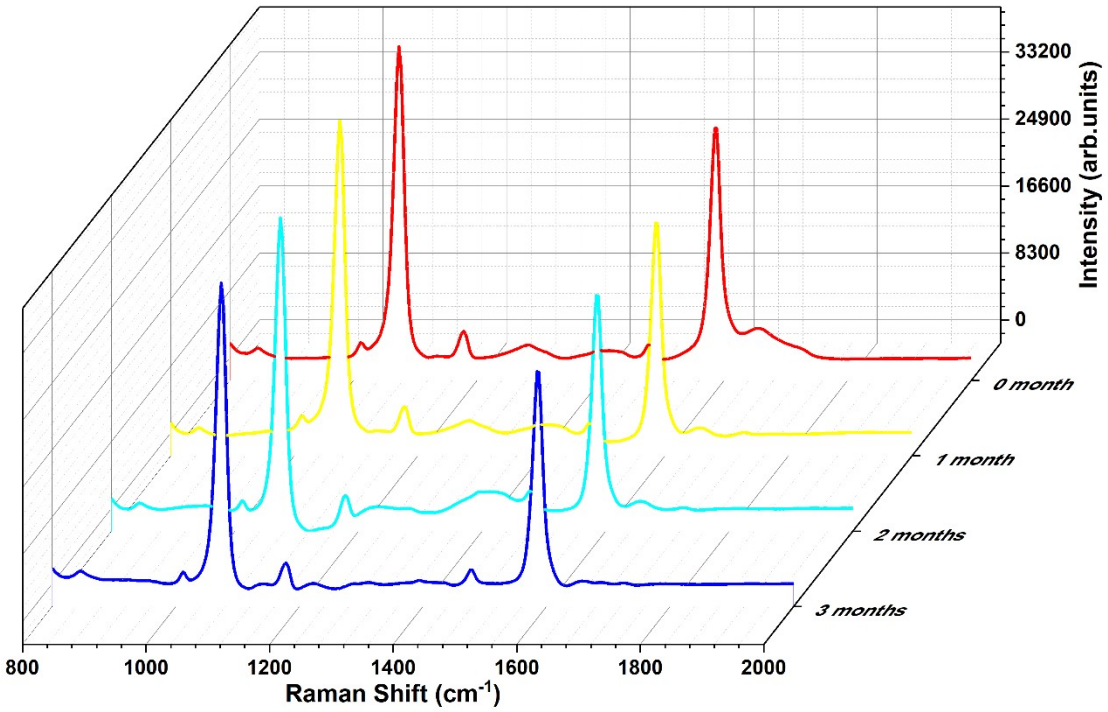

Figure S8. SERS spectra of 1.0 mM 4-MBA adsorbed on the P(4VP-*co*-DVB)/AuNPs nanocluster measured every month during three months.

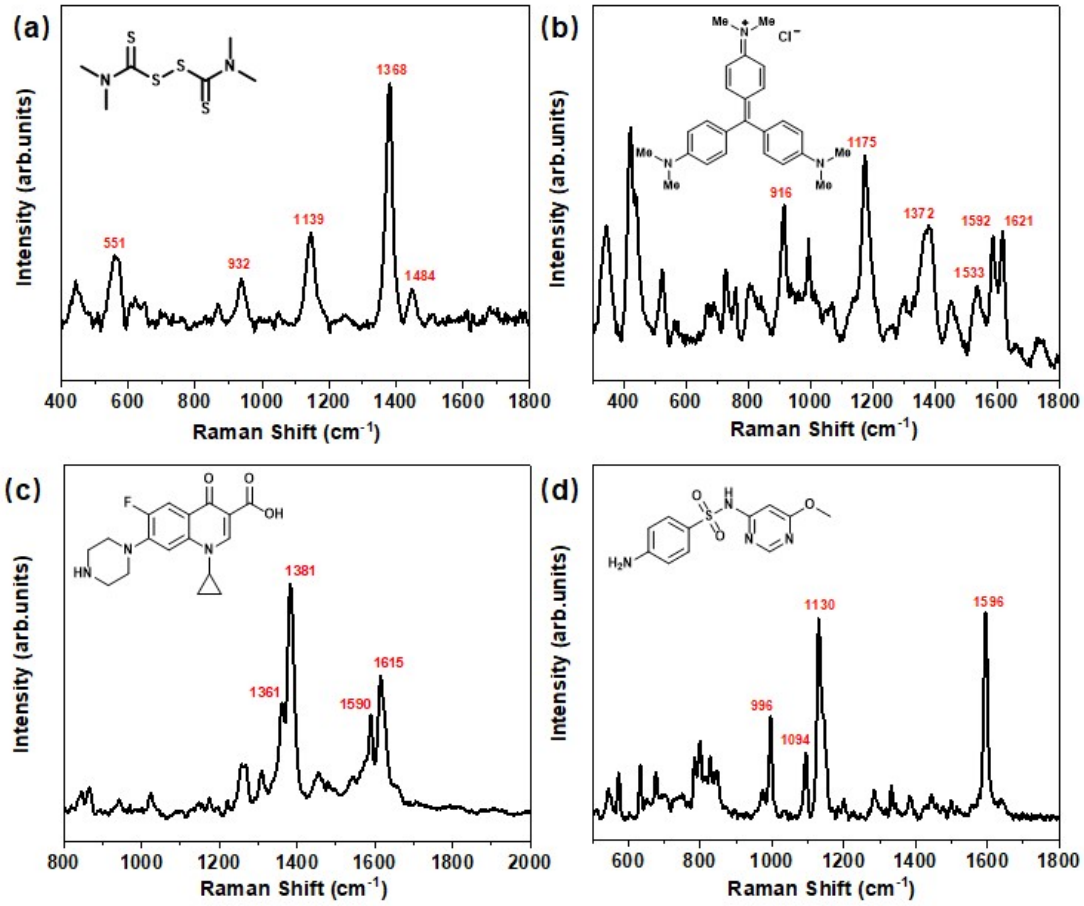

Figure S9. SERS spectra of (a) thiram, (b) crystal violet, (c) ciprofloxacin, and (d) sulfamonomethoxine with the concentration of 1.0 mM absorbed on the P(4VP-*co*-DVB)/AuNPs.

Table S1. Interparticle distance measurement of of SiO_2-*g*-P(4VP-*co*-DVB)/AuNPs in nm. STD DEV – standard deviation, RSDEV – relative standard deviation, St Error – standard error.

sample / Number	1	2	3	4	5	6	7	8	9	10
1	9.58	12.38	10.23	9.96	10.40	13.83	17.24	12.46	9.53	12.18
2	9.46	15.11	10.27	9.13	10.96	10.21	9.74	10.83	10.88	12.14
3	14.53	10.12	9.84	13.73	13.14	10.86	14.40	14.13	10.80	10.74
4	13.21	13.95	14.62	12.47	10.31	9.31	13.10	10.02	10.94	10.21
5	13.27	9.44	11.87	10.83	9.58	10.75	10.63	10.30	12.79	10.48
6	13.03	10.65	11.60	16.41	12.41	12.09	10.49	9.79	14.51	9.56
7	10.83	13.41	12.78	10.59	10.16	10.00	10.87	9.64	16.81	9.27
8	13.95	11.21	10.77	10.91	10.84	10.60	9.77	9.83	13.04	6.41
9	8.54	10.89	13.31	12.55	9.38	14.82	10.96	10.97	13.21	15.01
10	19.64	10.57	8.78	8.94	8.71	11.71	12.73	11.26	10.19	14.92
11	14.01	9.73	9.65	13.64	10.49	13.61	11.20	14.19	12.01	10.09
12	10.68	9.61	14.95	12.53	14.94	9.95	13.90	10.83	14.82	10.85
13	9.84	13.18	10.50	10.82	15.73	12.19	10.05	12.99	12.10	13.50
14	9.78	11.41	10.73	15.01	10.94	10.10	10.09	14.00	10.03	12.63
15	12.16	10.31	11.20	10.05	12.11	11.98	13.04	10.64	10.98	11.79
Average	12.17	11.46	11.40	11.83	11.34	11.46	11.88	11.45	12.17	11.31
MIN	8.54	9.44	8.78	8.94	8.71	9.31	9.74	9.64	9.53	6.41
MAX	19.64	15.11	14.95	16.41	15.73	14.82	17.24	14.19	16.81	15.01
STD DEV	2.845	1.744	1.802	2.172	1.994	1.622	2.140	1.653	2.040	2.238
RSDEV	0.234	0.152	0.158	0.184	0.176	0.142	0.180	0.144	0.168	0.198
St Error	0.735	0.450	0.465	0.561	0.514	0.418	0.552	0.427	0.526	0.577

Table S2. Interparticle distance measurement of P(4VP-*co*-DVB)/AuNPs in nm. STD DEV – standard deviation, RSDEV – relative standard deviation, St Error – standard error.

Number / sample	1	2	3	4	5	6	7	8	9	10
1	1.70	2.94	1.46	2.67	1.85	1.42	2.39	0.94	1.11	2.15
2	1.90	2.30	0.94	1.45	2.51	2.10	1.23	1.98	2.82	1.31
3	1.93	2.04	0.84	1.14	2.10	2.98	2.75	1.93	1.01	1.29
4	2.14	2.46	1.02	1.04	1.35	1.42	2.76	1.39	2.31	1.19
5	2.89	1.34	3.01	2.11	1.10	1.52	1.83	1.41	2.12	1.44
6	1.72	1.79	2.77	0.98	2.56	1.19	2.32	2.64	1.32	0.96
7	1.09	0.91	2.45	0.90	2.31	1.50	0.91	2.89	1.51	2.23
8	2.29	1.02	1.12	0.67	1.85	1.71	1.81	1.70	0.99	1.13
9	3.06	1.13	1.64	1.45	0.87	2.65	1.31	1.90	1.76	1.41
10	2.24	1.26	1.01	1.87	1.80	1.96	1.12	0.93	1.92	2.72
11	1.17	2.45	2.65	2.78	1.12	1.94	1.04	2.55	1.69	2.08
12	0.98	2.29	1.98	2.41	1.00	2.19	1.60	2.14	0.88	2.10
13	1.34	1.76	1.31	2.98	0.97	2.51	2.14	1.34	1.04	1.17
14	1.11	1.22	1.15	1.32	1.64	1.10	2.87	1.79	2.11	1.63
15	2.13	1.29	2.55	1.19	1.60	1.19	1.30	2.04	2.09	1.41
Average	1.846	1.747	1.73	1.664	1.642	1.825	1.825	1.838	1.645	1,615
Min	0.98	0.91	0.84	0.67	0.87	1.1	0.91	0.93	0.88	0.96
Max	3.06	2.94	3.01	2.98	2.56	2.98	2.87	2.89	2.82	2.72
STD DEV	0.638	0.633	0.766	0.752	0.565	0.572	0.675	0.580	0.582	0.513
RSDEV	0.34	0.36	0.44	0.45	0.34	0.31	0.37	0.316	0.35	0.328
St Error	0.165	0.163	0.198	0.194	0.146	0.148	0.174	0.150	0.150	0.133

Table S3. Comparison of SERS enhancement properties with other nanostructures.

Sample	EF	Reference
AuNPs	2.24×10^4	[3]
Ag nanocubes	1.60×10^6	[4]
AuNP-AuNP nanoassemblies	2.00×10^6	[5]
AuAgNC-AuNP nanoassemblies	3.00×10^6	[6]
AuNPs/PSi	4.8×10^5	[7]
P(4VP-*co*-DVB)/AuNPs	1.42×10^7	This work

References

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